

**Zirconium and Titanium Nanoclusters for Use as an Ablative for Solid
Rocket Motor (SRM) Insulation.**

Final Report

(A) Supply of AFRL with nanoclusters:

About 225 g of $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ (OMc = methacrylate), 50 g of $\text{Hf}_4\text{O}_2(\text{OMc})_{12}$, 15 g of $\text{Ti}_6(\text{OEt})_8\text{O}_4(\text{OMc})_8$ and 6.5 g of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{propionate})_{12}(\text{PrOH})$ were synthesized and shipped in two batches to the AFRL in Edwards.

We tried to scale the synthesis of $\text{Zr}_4\text{O}_2(\text{methacrylate})_{12}$ from the previous 0.5 – 10 g scale up to larger amounts. The cluster is prepared by adding a 7-fold molar excess of methacrylic acid to a 80% solution of $\text{Zr}(\text{OBu})_4$ in n-butanol. After one day, the cluster crystallizes in quantitative yield. When we scaled the synthesis up to a 15 g batch of the cluster under the same conditions, we did not get crystals, but instead a gel-like mass. However, Raman and NMR spectra of the dried gels showed unequivocally that the amorphous solid also consists of the cluster $\text{Zr}_4\text{O}_2(\text{methacrylate})_{12}$, together with a small amount of residual butanol that could not be removed upon drying. Thus, an upscaling to larger quantities is possible, i.e. the synthesis procedure is reliable even on a larger scale, although the batch may not crystallize. The only problem arising from this fact is that the purity of an amorphous sample is more difficult to check, since X-ray diffraction cannot be applied in this case. The only relatively simple method is low-temperature ^1H - and ^{13}C -NMR spectroscopy, where an unequivocal "fingerprint" spectrum is obtained. At room temperature, the signals are averaged due to dynamic processes.

(B) New clusters:

The new clusters $\text{Hf}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}(\text{BuOH})$, $\text{Ti}_4\text{Hf}_4\text{O}_6(\text{OBu})_4(\text{OMc})_{16}$ and $\text{Ti}_2(\text{Zr/Hf})_6\text{O}_6(\text{OMc})_{20}$ were prepared. They are isostructural with the previously prepared zirconium clusters $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{12}$, $\text{Ti}_4\text{Zr}_4\text{O}_6(\text{OBu})_4(\text{OMc})_{16}$ and $\text{Ti}_2\text{Zr}_6\text{O}_6(\text{OMc})_{20}$.

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14. ABSTRACT This report describes the synthesis of metal oxide nanoclusters with a reactive corona of methacrylate groups. The metal oxide clusters investigated include zirconium, hafnium and titanium metal oxide nanoclusters. Methods of synthesis of metal nanoclusters with nonreactive corona were also investigated. The relatively high melting point of these materials makes them of interest for possible motor insulation applications.					
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The reason why we also prepared the Hf analogues was that hybrid polymers prepared from these clusters result in a larger inorganic residue when the same molar portion of cluster is used, due to the higher molecular mass of Hf compared to Zr. Apart from that, the hybrid polymers obtained from the Hf_6 cluster as the inorganic component and methylmethacrylate or styrene as organic co-monomers exhibit minor, but significant differences in the polymer properties.

(C) Metal nanoclusters with a non-reactive corona:

We did preliminary experiments aimed at synthesizing clusters with a reduced number of organic functionalities. Reducing the number of the double bonds around the cluster metal core would allow to tailor the crosslinking degree of the organic network and thus the polymer properties. Two different approaches were tested:

(1) We reacted $\text{Zr}(\text{OBU})_4$ with propionic acid instead of methacrylic acid the cluster $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{propionate})_{12}]_2$ was obtained. This acid was chosen because it has similar steric and ligand properties than methacrylic acid. Using a mixture of methacrylic acid (functional acid) and propionic or acetic acid (non-functional acids) resulted in the formation of mixed methacrylate/propionate- or methacrylate/acetate-substituted clusters. We were able to crystallize two of them, i.e. $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_9(\text{propionate})_3]_2$ and $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{6-x}(\text{acetate})_{6+x}]_2$ ($x = 0-3$). The structures of the three new clusters consist of two $\text{Zr}_6\text{O}_4(\text{OH})_4$ cluster cores, which are bridged by four propionate or acetate ligands. The other ligands cap the two $\text{Zr}_6\text{O}_4(\text{OH})_4$ units. This structure type was previously observed for $[\text{Zr}_6(\text{OH})_4\text{O}_4(\text{acrylate})_{12}]_2$. In the case of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OMc})_{6-x}(\text{acetate})_{6+x}]_2$, the exact number of acetate or methacrylate ligands cannot be determined due to disorder of the carboxylate ligands. The composition of the new clusters shows that (i) the cluster type is retained for different carboxylate ligands with similar steric and electronic properties, (ii) using mixtures of carboxylic acids does not necessarily lead to a mixture of differently substituted clusters but can indeed result in clusters of a uniform stoichiometry with two different carboxylate ligands, and (iii) the reactive ligands in the parent cluster $\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}$ (or the corresponding acrylate derivative) can be successively replaced by non-reactive ligands.

We are still working on getting clusters with different ratios between functional and non-functional carboxylate ligands.

(2) The reactive methacrylate groups at the cluster surface can be used to modify the ligand properties. When the cluster $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ was reacted with a stoichiometric amount of HSiPh_3 in the presence of $\text{PtCl}_2(\text{PhCN})_2$ as the catalyst (Speier's catalyst did not work), all methacrylate were hydrosilylated to give saturated ligands. Experiments with smaller amounts of HSiPh_3 are on the way to test the possibility of *partial* blocking of the methacrylate ligands.

(3) A third possibility to reduce the number of reactive groups at the cluster surface is an exchange of the reactive carboxylate ligands by non-reactive ones. This possibility was checked by NMR exchange experiments. When $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ was reacted with two equivalents methacrylic acid, an exchange process involving the acid molecules was observed. We then extended our studies to other carboxylic acids in order to investigate how and at which extent this exchange could lead to clusters with two different ligands. With both benzoic and 2-bromoisobutyric acid a rapid exchange was observed when two molar equivalents were added to the $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ solution. These NMR spectroscopic observations are a very promising onset for exchange reactions on a preparative scale.

Declarations

(1) The Contractor, Vienna University of Technology, hereby declares that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. F61775-02-WE037 is complete, accurate, and complies with all requirements of the contract.

Vienna, December 4, 2002



Prof. Dr. Ulrich Schubert

(2) I certify that there were no subject inventions to declare as defined in FAR 52.227-13, during the performance of this contract.

Vienna, December 4, 2002

A handwritten signature in black ink, appearing to read 'U. Schubert', written in a cursive style.

Prof. Dr. Ulrich Schubert